Review

Combinatorial search for oxygen reduction reaction electrocatalysts: A review

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HIGHLIGHTS

► High-throughput screening techniques for ORR electrocatalysts were reviewed.
► Four major screening techniques were introduced.
► Merits and limitations of each technique were discussed along with recent results.

ARTICLE INFO

ABSTRACT

Oxygen reduction reaction (ORR) is one of the most interesting research issues in the academia and industries due to its importance in polymer electrolyte membrane fuel cells. Development of new ORR catalysts with low cost and high activity is under intensive research, but it is a time-consuming process because of wide range of alloys to be explored. Combinatorial synthesis and high-throughput screening techniques were suggested as new experimental approaches to accelerate the ORR electrocatalyst research. The combinatorial method is focused on the synthesis of concentrated arrays and quick evaluation of the arrays *via* various screening techniques. In this report, the combinatorial approaches for the ORR catalyst research were reviewed based on the screening methods. Four screening techniques of optical screening, scanning electrochemical microscopy, multielectrode half cell, and multielectrode full cell were introduced as the representative ones. Other approaches were also briefly introduced. Merits and limitations of each method were discussed and representative research results of each method were shown in detail.

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1. Introduction

Oxygen reduction reaction (ORR) electrocatalyst has been an attractive research issue due to its application to a cathode material for polymer electrolyte membrane fuel cells (PEMFCs). In addition, Whitesides and Crabtree [1] have pointed out the oxygen electrode problem as one of the nine representative long-term research issues that are critical for future energy technology. The PEMFCs produce electricity and water through an electrochemical reaction of hydrogen and oxygen that are supplied to the anode and cathode, respectively [2]. As PEMFCs do not produce any greenhouse gases, they are considered as a promising alternative to combustion engines. However, commercialization of the PEMFCs is still underway because of various obstacles such as high cost, low

performance, and durability issues. One of the most troublesome technologies is the cathode electrode, where oxygen is reduced to water as follows:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (1)$$

Carbon supported Pt is widely used as the cathode electrocatalyst for ORR, but its high cost combined with low catalytic activity is pointed out as one of the major barriers in the commercialization of PEMFCs. Although intensive researches were performed to develop highly active and low-cost ORR electrocatalysts, approximately four times higher ORR activity per precious metal mass is still required in comparison to that of conventional Pt catalysts for the commercialization of PEMFCs [3,4]. The cost/activity issues are identically applied to other energy application areas such batteries, pyroelectrochemical process even in nuclear energy, etc., where high-priced noble metal-based catalysts are used as electrode materials.

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Consequently, major efforts for the development of Pt-based ORR electrocatalysts with high performance were devoted to transition metal doped Pt-based binary alloys including PtCo [5–9], PtFe [10,11], PtCr [12,13], PtNi [9,14,15], and PtTi [16–18]. Although various binary catalysts have been examined, there are still a lot of alloys to be explored. For example, Greeley et al. [19] recently suggested a new Pt_3Y catalyst as a promising ORR catalyst *via* density function theory calculations and high ORR activity was confirmed by experimental results [19,20]. In addition, some ternary electrocatalysts (such as Re–Pt/Pd [21], Pt–Co–Cr [22–26] alloys) showed promising ORR activities suggesting that it is worth expanding target materials even wider than before. However it is a time-consuming process to search for new combinations and to optimize their compositions. When it comes to ternary compounds, there are 66 compositions to be explored to find an optimum composition even when 10% of composition step is applied. Therefore, it is reasonable to employ an accelerated experimental technique to reduce time and cost for the catalyst development. From this point of view, combinatorial synthesis and high-throughput screening techniques were first introduced to the electrocatalyst field by Reddington et al. [27] for methanol electro-oxidation reaction (MOR). The authors prepared a 645-membered electrode array which contained binary, ternary, and quaternary combinations of Pt, Ru, Os, Ir, and Rh. The highest MOR activity was observed in the composition of Pt(44)/Ru(41)/Os(10)/Ir(5).

Combinatorial search for the fuel cell electrocatalysts was accelerated especially for the MOR electrocatalysts since this report [28–36]. However, relatively fewer reports were published for the ORR electrocatalysts, which might be because of more limitations in the evaluation of ORR activity than that of MOR activity. Generally rotating disk electrode (RDE) technique is employed for electrochemical evaluation of the ORR activities because of low solubility of oxygen in the electrolyte solution (H_2SO_4 or $HClO_4$) [37]. Thus, in the RDE experiments, a working electrode has to be rotated at a high speed to continuously provide oxygen to the electrode surface. On the other hand, in the case of MOR, methanol is easily mixed with the electrolyte solution and rotation of the electrode is not essential. Although RDE technique is a well-established method for the evaluation of the ORR activity, it is not applicable for combinatorial libraries which cannot be rotated generally. However, recent reports suggest that the combinatorial synthesis and high-throughput evaluation techniques can be successfully employed for the development of new ORR electrocatalysts.

As noted above, the key technique in the combinatorial search for the ORR electrocatalyst is the development of the high-throughput screening method. Therefore, in this report, recent efforts on this subject are reviewed based on the screening methods.

2. Literature results and discussion

2.1. Optical screening

Optical screening was the initial approach in the combinatorial method for MOR electrocatalysts due to its easy operation and quick evaluation characteristics [27]. In this technique, a pH indicator, which emits fluorescence at a certain range of pH, is added to an electrolyte solution. For the MOR, pH decreases as the following reaction proceeds.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{2}$$
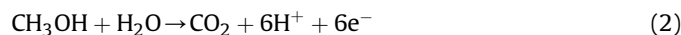
While, the pH increases when the ORR proceeds because protons are consumed by Eq. (1). Thus, the optical screening

method can be employed for the evaluation of ORR electrocatalysts using a pH indicator which emits fluorescence when pH is increased by the progress of ORR.

Chen and co-workers [38] employed Phloxine B as an indicator to identify the ORR activity of an array that consisted of combinations of Pt, Ru, Os, Ir, and Rh. The array was fabricated by a liquid dispensing method, which spots precursor solutions on a conductive substrate (Teflon-coated Toray carbon sheet was used in this study). The catalyst spots were reduced by adding $NaBH_4$ solution to each spot. In this study, the authors identified $Pt_{4.5}Ru_4Ir_{0.5}$ as the best catalyst for both the ORR and water oxidation reaction.

Liu et al. [39] also employed the optical screening method for quick evaluation of two binary catalyst arrays; one of which was a Pt-based array (81 compositions) and the other one was a non-Pt array (90 compositions). In this report, the authors employed fluorescein as an indicator which can operate at a pH of 4 instead of 2.7 (Phloxin B). The screening results are shown in Fig. 1(a) and (b) for the Pt-based and non-Pt arrays, respectively [39]. In the Pt-based array, Pt–Bi and Pt–Se binary compositions exhibited high ORR activities, while RuFe did in the non-Pt array. The identical condition was employed by Jeon et al. [40] to search for methanol tolerant ORR electrocatalysts. In this study, the best composition Pt(50)Ru(20)Fe(20)Se(10) was also investigated in its powder version, which also exhibited excellent methanol tolerance. But the Pt(50)Ru(20)Fe(20)Se(10) catalyst showed a fast degradation during the potential
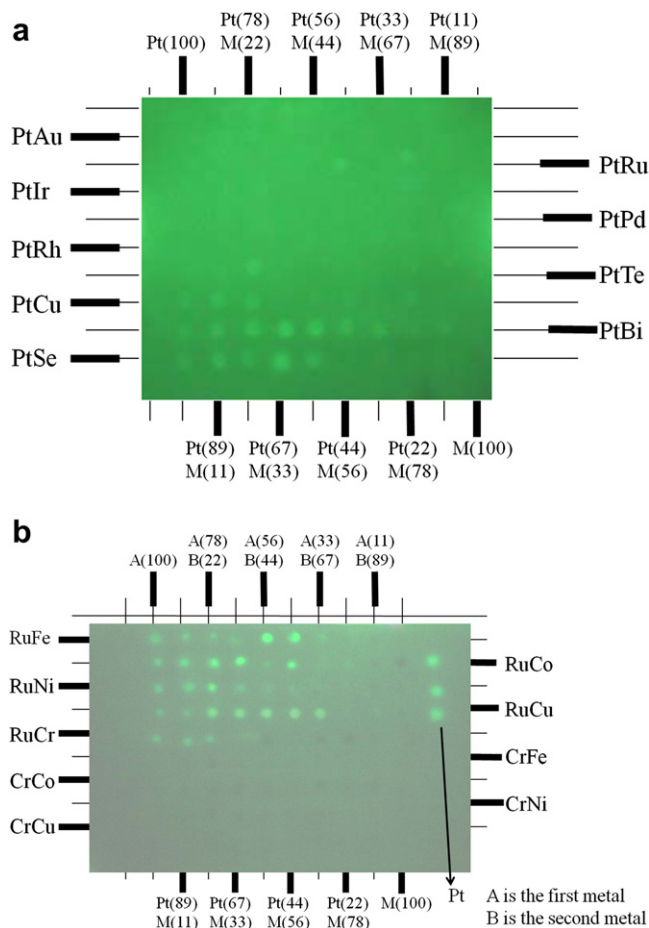

Fig. 1. The optical screening results of the (a) Pt-based and (b) non-Pt binary arrays. The fluorescence image was taken at 0.55 V (vs. reversible hydrogen electrode) using oxygen saturated sulfuric acid solution (pH 4) as the electrolyte solution, which also contained 100 μM of fluorescein and 0.2 M $NaNO_3$. (Reproduction of Figs. 3 and 7 of [39] for (a) and (b), respectively.)
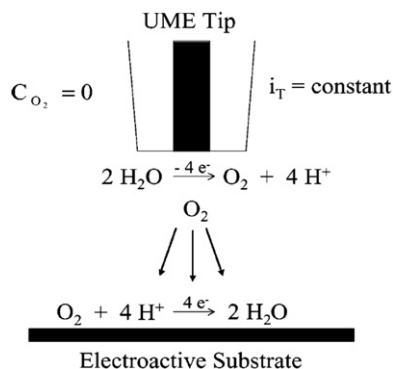
Fig. 2. Schematic figure of the TG-SC mode SECM operation for the ORR activity evaluation. (Reprinted with permission from [41]. Copyright 2003 American Chemical Society.)

cycling, which might be due to the dissolution of Se. This behavior could not be identified in the library evaluation. Although fluorescein can operate at a higher pH range than Phloxine B, it should be mentioned that NaNO$_3$ was added to the electrolyte solution in the case of Refs. [39,40] to maintain conductivity of the electrolyte. Operating at a higher pH brings an advantage of easy detection of activity because far less amount of proton consumption is required at higher pH range, which means fluorescein is more sensitive to the proton consumption. But, effect of NaNO$_3$ on the catalysts is not clear yet indicating that there can be catalyst–NaNO$_3$ interaction which can affect the screening results. Therefore, more investigation should be addressed on this issue.

As shown above, the optical screening method provides an easy and quick evaluation of the combinatorial libraries, while it has weaknesses of indirect measurement of the activity and quite different condition of evaluation (pH and effect of indicator and/or NaNO$_3$). To avoid misled conclusion caused by the weaknesses of the optical screening method, a viable approach is synthesis and characterization of the optimum composition identified by the optical screening method *via* traditional ways including RDE testing.

2.2. Scanning electrochemical microscopy (SECM)

The SECM technique for the ORR electrocatalyst was first introduced by Fernández et al. [41,42]. They employed a tip
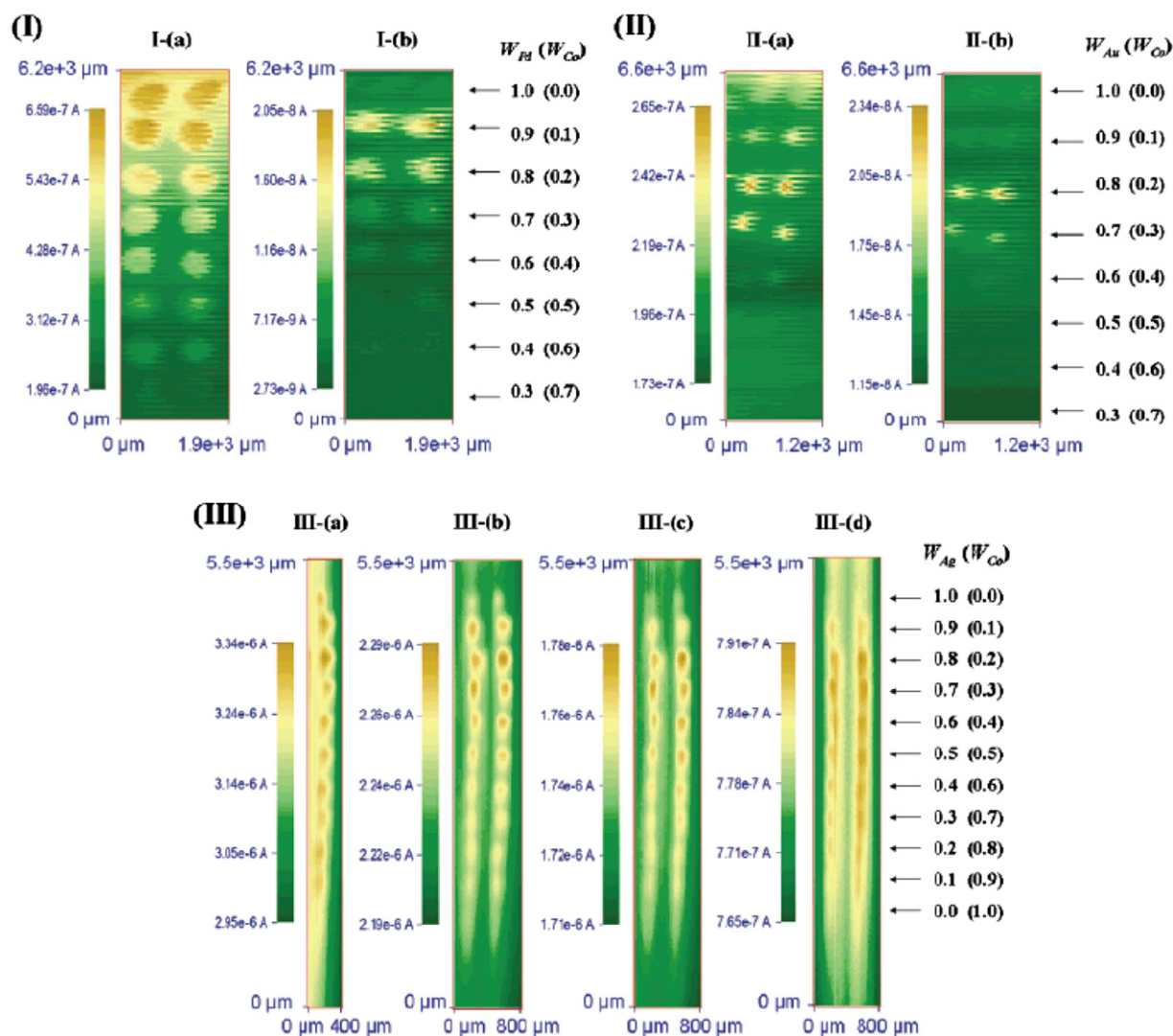

Fig. 3. The SECM images of (I) Pd–Co, (II) Au–Co and (III) Ag–Co binary arrays. Measurement was performed in a 0.5H$_2$SO$_4$ electrolyte solution. Tip-substrate distance was 30 μm and tip current was −160 nA. (I) Pd–Co system with a scan rate of 50 μm each 0.2 s, (I-a) E_S = 0.4, (I-b) E_S = 0.7 V (vs. RHE), (II) Au–Co system with a scan rate of 50 μm each 0.2 s, (II-a) E_S = 0.2, (II-b) E_S = 0.4 V (vs. RHE), and (III) Ag–Co system with a scan rate of 20 μm each 0.017 s, (III-a) E_S = −0.05, (III-b) E_S = 0.05, (III-c) E_S = 0.15, and (III-d) E_S = 0.2 V (vs. RHE). E_S and W_M represents substrate potential and atomic ratio of each metal, respectively. (Reprinted with permission from [42]. Copyright 2005 American Chemical Society.)
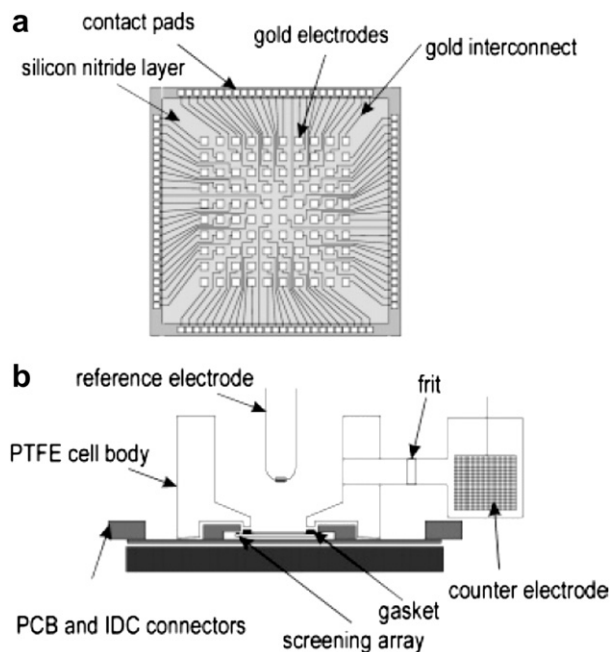
produce oxygen. Then oxygen diffuses to the substrate so that the ORR occurs on the substrate. Scanning results of Pd–Co, Au–Co, and Ag–Co binary alloys are shown in Fig. 3. In the Pd–Co array, the ORR activity was observed up to 70 at.% Co when 0.4 V (vs. reversible hydrogen electrode, RHE) was applied to the substrate (All potentials in this report were converted into RHE scale). When the substrate potential increased to 0.7 V, Pd(90)Co(10) composition exhibited the highest ORR activity. In addition, pure Pd did not show ORR activity while the Pd–Co binary catalysts (Co more than 20 at.%) showed ORR activities decreasing with an increase in the Co concentration. In the Au–Co binary array, Au(70)Co(30) composition exhibited the highest ORR activity at 0.2 and 0.4 V of substrate potentials. In the Ag–Co array, the ORR activity of Ag decreased to zero as the substrate potential increased from −0.05 to 0.2 V. On the other hand, Ag–Co binary compositions maintained their activity at 0.2 V, and the highest ORR activity was observed in Ag(80)Co(20) composition. The high ORR activities observed in the Pd–Co array were also confirmed by the RDE technique suggesting that the SECM technique is a useful method in fast screening of the arrays.

Walsh et al. [43] selected promising combinations based on a thermodynamic guide. Four binary catalyst arrays including Au–V, Ag–V, Pd–Mn, and Pd–V were prepared by the liquid dispensing technique. At initial screening, Pd(60)V(40) composition was identified as a highly active ORR catalyst. And the identical composition was also investigated in a carbon supported powder version, which resulted in high ORR activity close to Pt, indicating that the new catalyst is a promising non-Pt ORR catalyst.

Lu et al. [44] employed sputtering methods to prepare a combinatorial library while the above mentioned works [41–43] employed the liquid dispensing method. In this work, they showed that the SECM technique is applicable to continuous composition substrates with a mapping of the ORR activities, meaning that much more compositions can be identified by the SECM technique when it is combined with a more concentrated array preparation technique.
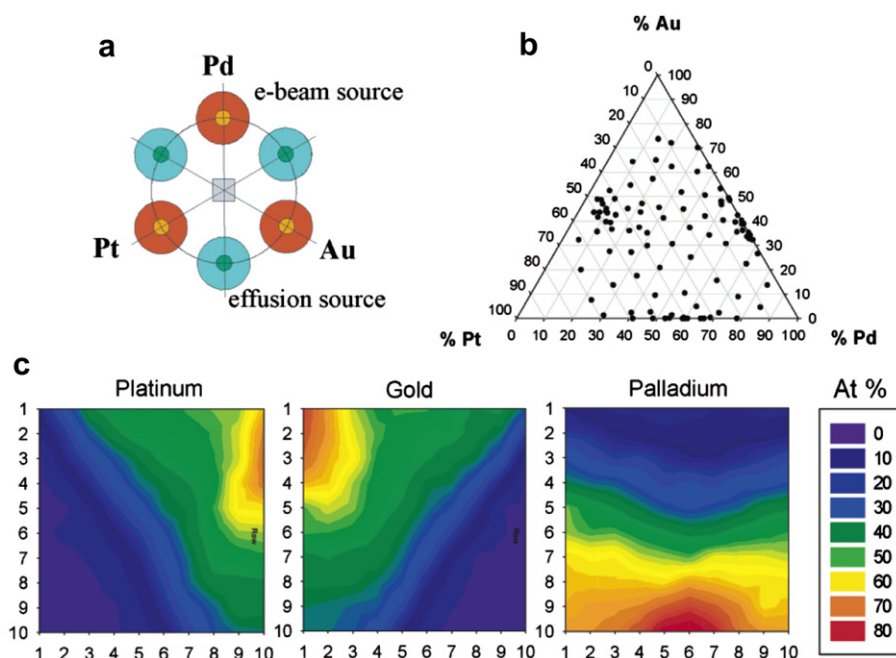

Fig. 4. Schematic drawings of (a) 10 × 10 working electrode array and (b) electrochemical testing cell set-up. (Reprinted with permission from [46]. Copyright 2006 American Chemical Society.)

generation-substrate collection (TG-SC) mode SECM to evaluate the ORR activity. Schematic diagram of the TG-SC mode is shown in Fig. 2. In this mode, a fixed potential high enough to reduce oxygen is applied to the substrate. As an oxygen-free electrolyte is used, a negligible current flows in the substrate. At the same time, ultramicroelectrode (UME) is positioned close to the substrate while applying a fixed oxidation potential to oxidize water to

Fig. 5. (a) Location of metal sources employed in the high-throughput physical vapor deposition system. (b) Composition map of the deposited array. (c) Composition contour map of each component on the square array substrate resulting from (b). (Reprinted with permission from [46]. Copyright 2006 American Chemical Society.)
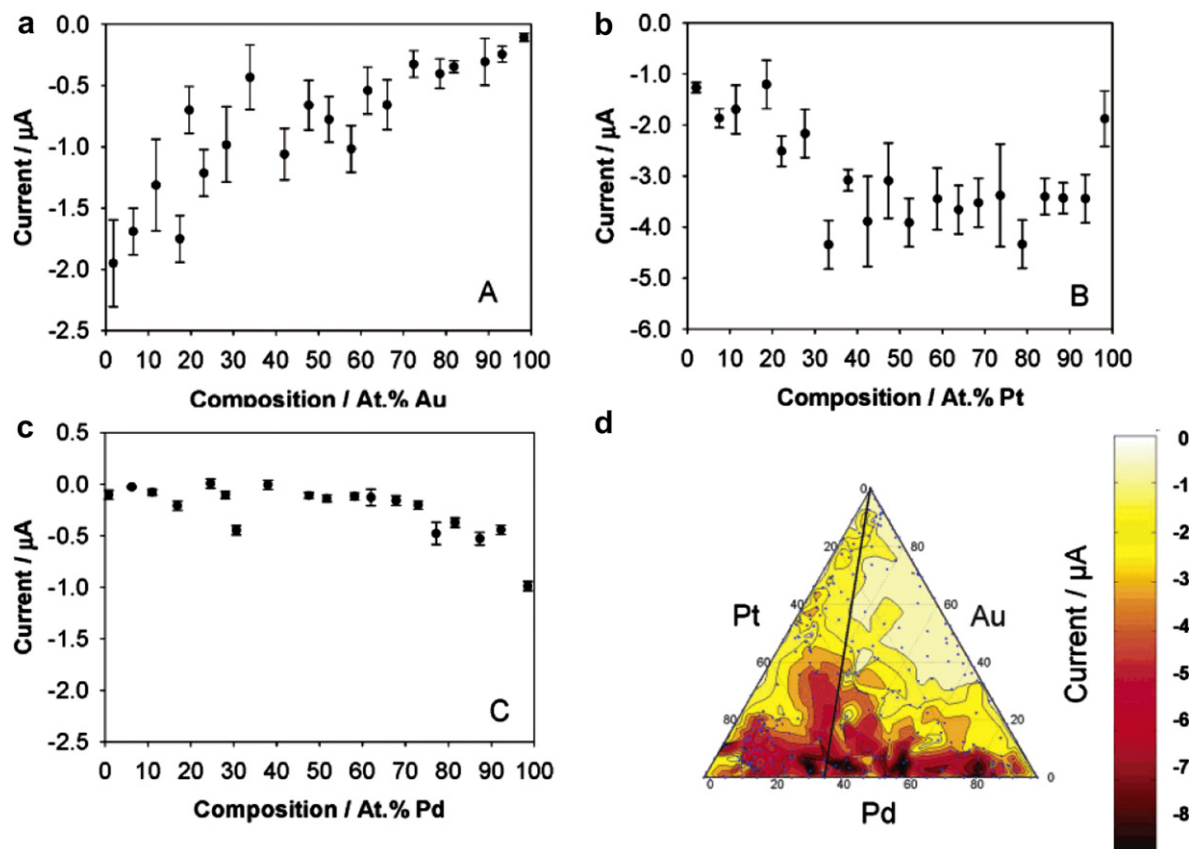
Fig. 6. Steady-state ORR activity of (a) PtAu, (b) PdPt, (c) AuPd, and (d) PtAuPd combinations at 0.80 V (vs. RHE). 0.5 M HClO$_4$ solution was employed as the electrolyte. (Reprinted with permission from [46]. Copyright 2006 American Chemical Society.)

As shown above, the SECM technique looks successful in terms of a quick evaluation of the arrays as the optimum compositions identified by this method were in good agreement with powder version results. In addition, this method can be more powerful when a concentrated array is prepared as Lu et al. [44] have shown. But as the previous works mentioned [41–43], the activity identified by this method still needs to be confirmed *via* traditional methods.
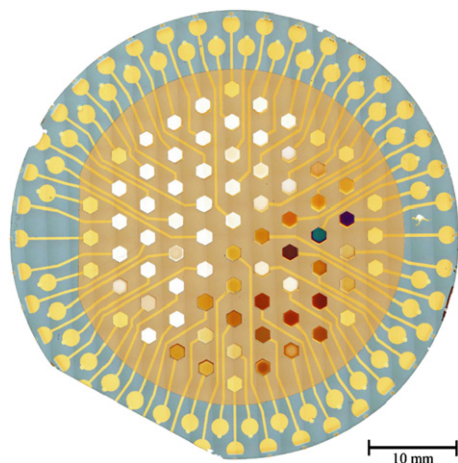

Fig. 7. A picture of combinatorial library fabricated on a silicon wafer. (Reproduction of Fig. 1 of [25].)

2.3. Multielectrode half cell

This technique is widely used due to its merits of respective control and evaluation of each spot, and direct measurement of ORR current. But this method requires well-fabricated arrays, where catalyst spots are generally deposited by a physical vapor deposition system on a substrate which has electrical lids to each spots to provide a respective control on each spot. In addition, quick evaluation of this system requires a multi-channel potentiostat to measure the ORR activity of each spot simultaneously.

Guerin et al. [45] fabricated a 10 × 10 gold array (1 mm × 1 mm for each spot) on a silicon wafer which has individual electrical connection for each spot. They investigated the ORR activity based on the particle size of each electrode including the effect of support materials (TiO$_x$ or C). They observed that the ORR activity was not improved when particle size is larger than 3.0 nm, while the activity rapidly decreased when particle size is smaller than 3.0 nm. Guerin et al. [46] also investigated binary Pt–Pd and ternary Pt–Pd–Au systems for the ORR. A 10 × 10 array of 1 mm^2 gold electrodes was fabricated on a 36 mm^2 of Si (1 mm thick). Each electrode was connected to a contact pad so that potentiostat can control each electrode. Except for Au contact pads and electrodes, the array was passivated by silicon nitride. A schematic diagram is shown in Fig. 4. Composition gradient was generated by depositing Pt, Pd, and Au simultaneously in a specially designed chamber where each target was off-centered so that ternary compositions are produced as each metal is deposited with different ratios at each position. The formation of concentration gradient is well
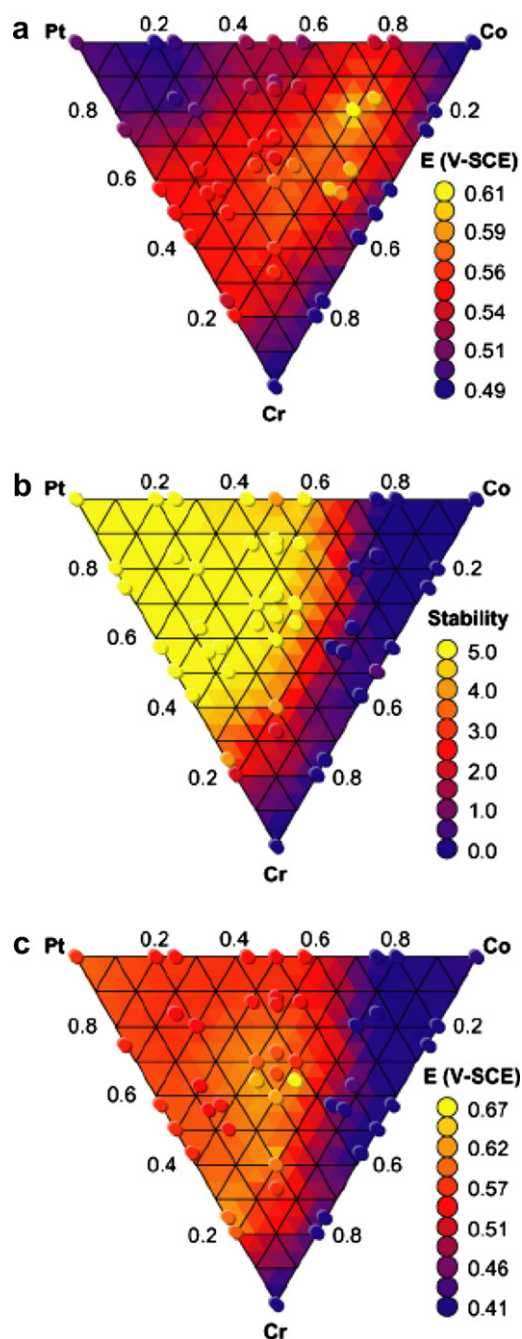
Fig. 8. The electrochemical testing results of the Pt–Co–Cr combinatorial array. (a) Initial on-set potential measured during the 10th downward sweep. (b) Visually evaluated corrosion score. (c) On-set potential after prolonged testing. The measurement was performed in an oxygen saturated 0.5 M H_2SO_4 solution as the electrolyte at a scan rate of 10 mV s^{-1} and at room temperature. (Reproduction of Fig. 6 of [25].)

potentiostat for simultaneous evaluation of the arrays. For the evaluation of the arrays, oxygen was bubbled through the electrolyte solution (0.5 M H_2SO_4) and ORR activity was measured during the potential cycling. In the Pt–Ru array, the addition of Ru worsened the ORR activity meaning that pure Pt exhibited the highest ORR activity in the binary Pt–Ru system. Among the ternary alloys, Pt(28)Co(36)Cr(36) catalyst showed the highest ORR activity based on on-set potential. The evaluation results of the Pt–Co–Cr array are shown in Fig. 8.

Despite of the advantages of the multielectrode half cell method, depletion of oxygen on the catalyst surface caused by the fixed testing station still remains as a limitation. In addition, the fabrication of an array for this technique requires somewhat expensive and complicated instruments for the substrate preparation and the catalyst deposition processes when compared with other techniques mentioned above.

2.4. Multielectrode full cell

This method was first introduced by Smotkin et al. [47] to provide a real fuel cell environment for simultaneous evaluation of various catalysts. In this study, the authors fabricated an electronically insulating block which has a serpentine flow field and 5×5 holes where graphite electrodes can be inserted. A 5×5 catalyst array was formed on a Nafion membrane, which was sandwiched by the 5×5 electrode block and another block which have 5×5 holes to work as a counter/reference electrode. For the counter/reference electrode, Pt was deposited on the backside of Nafion membrane where 5×5 electrodes were deposited. The array components and structures are shown in Fig. 9. The ORR activity was measured by flowing humidified air at the array side and humidified hydrogen at the counter/reference electrode side. The evaluation results of 25 Pt spots are shown in Fig. 10. As shown in the figure, a reasonable repeatability was revealed for the 25 Pt/C catalyst spots. This method might not need further confirmation of the catalytic performance, while it clearly needs more improvements especially in the array fabrication method and number of catalyst spots that can be evaluated simultaneously. In addition, it should be mentioned that there can be decontamination or concentration effect during the evaluation process because the catalyst spots share a flow stream of reactants. Another weakness of this technique is a lack of publications for other cases. Yu and Pickup [48] have employed this technique for the evaluation of formic acid electro-oxidation reaction using a 3×3 array, which showed that this technique is useful to show a trend of activity. Therefore, it is clear that more results should be provided for this technique to be accepted as a reliable method for the ORR catalyst research.

2.5. Other approaches

Easton et al. [49,50] employed a slightly different technique in the synthesis and evaluation of combinatorial arrays. A specially designed magnetron sputtering system was employed for the fabrication of combinatorial array as shown in Fig. 11. Fe–C–N ternary composition was generated using C and Fe targets and Ar balanced nitrogen gas was fed during the deposition. As shown in the figure, each target can generate concentration gradient along the radial direction. Films of Fe–C–N were deposited onto quartz strips, Si wafer, Al disks, and 15 glassy carbon disks. The glassy carbons were mounted as three sets of 5 electrodes. Evaluation of the catalysts deposited on the glassy carbon electrodes was performed by conventional rotating ring-disk electrode technique, and the results are shown in Fig. 12. In this study, meaningful results
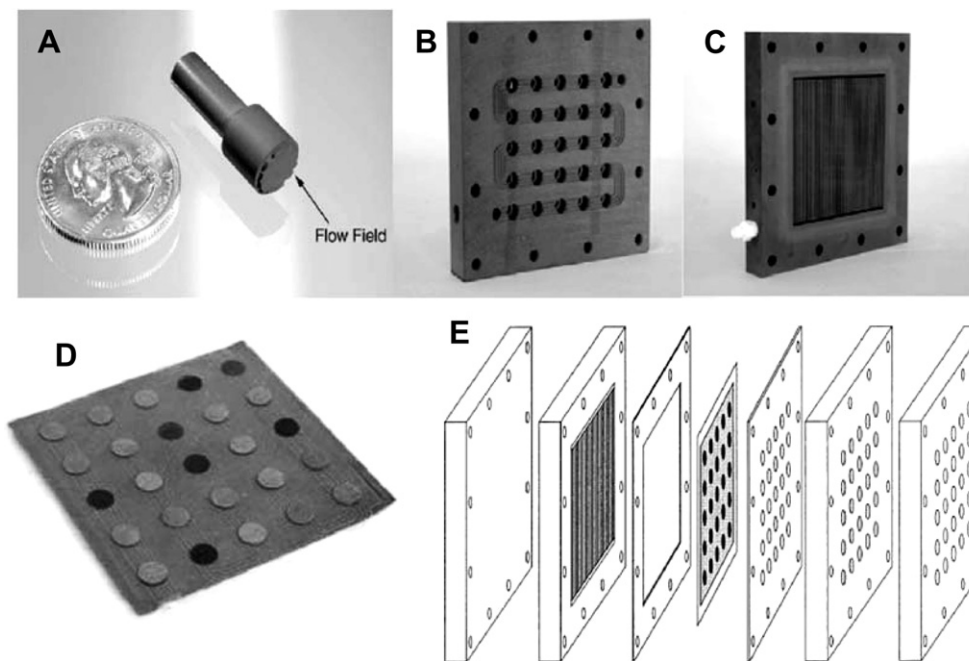
described in Fig. 5. The ORR activity evaluation results of the Pt–Pd–Au array are shown in Fig. 6, where high ORR activity was observed near Pt(80)Pd(20) and Pt(70)Pd(30) regions.

Cooper and McGinn [25] fabricated binary and ternary composition arrays including Pt–Ru, Pt–Co–Ti, Pt–Co–Cu and Pt–Co–Cr by employing plasma sputtering technique. The arrays contained 63 different compositions which were generated using 6 different shadow masks during the sputtering process. An example of the array is shown in Fig. 7. They employed a commercial 100 channel

Fig. 9. Components of the multielectrode full cell. (A) Graphite electrode which is going to be connected to a potentiostat. (B) Flow field block which is electronically insulating. The graphite electrodes (A) are inserted into the holes. (C) Counter/reference electrode block. (D) 5×5 catalyst array. The catalysts were deposited on a Nafion membrane. (E) The entire multielectrode full cell assembly. (Reproduction of Fig. 2 of [47].)

were achieved from the $Fe_xC_{1-x-y}N_y$ compositions when $0 < x < 0.035$ and $0.01 < y < 0.16$.

He et al. [17,52] adopted a similar approach with that of Easton et al. [49,50]. They have deposited thin film catalysts by a multi-source physical vapor deposition system. This system has 12 plasma guns and can deposit up to 4 elements simultaneously. A multi-channel RDE system was employed for the evaluation of the library. This evaluation system consists of 16 stations, and each has a conventional rotator, a glass cell, a counter, and a reference electrode. Each working electrode was tested in an individual glass cell to avoid cross-contamination which can be caused by the

dissolution of non-noble metals under acidic conditions. By this method, the authors have explored various binary [17] and ternary [52] systems. In the binary system, PtW, PtTi, and PtSe were suggested as promising candidates, and PtTiNi, PtTiCu, and PtTiV exhibited higher ORR activities in the ternary system.

The two examples mentioned in this section do not have special benefits in the evaluation process, while they are attractive for their quick synthesis of combinatorial arrays. But it is clear that these methods might have their strength in reliability. It might be worth considering the combination of multielectrode full cell systems with these methods so that merits of each method can be combined.
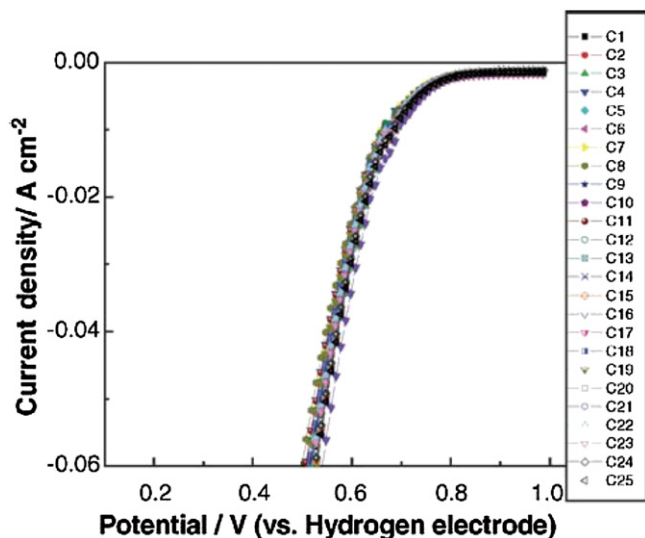

Fig. 10. The ORR activity measurement curves of 25 identical Pt/C catalysts. The experiment was performed at 60 °C by flowing 1000 SCCM humidified air at the working electrode side and 200 SCCM humidified hydrogen at the counter/reference electrode side. (Reproduction of Fig. 6(a) of [47].)
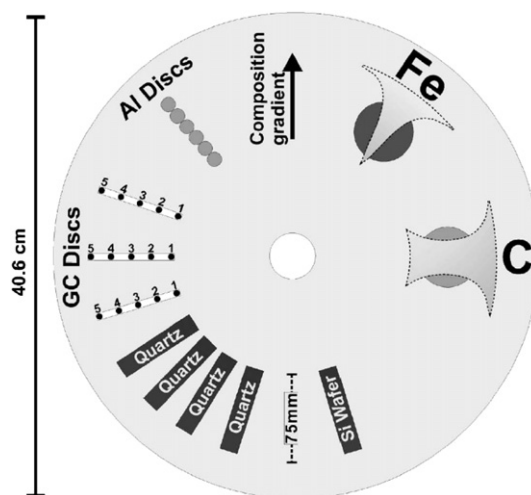

Fig. 11. Schematic diagram of the rotating substrate table. Projections of the Fe and C targets are shown with the masks which generates composition spread. (Reproduction of Fig. 1 of [49]. Reproduced by permission of The Electrochemical Society.)
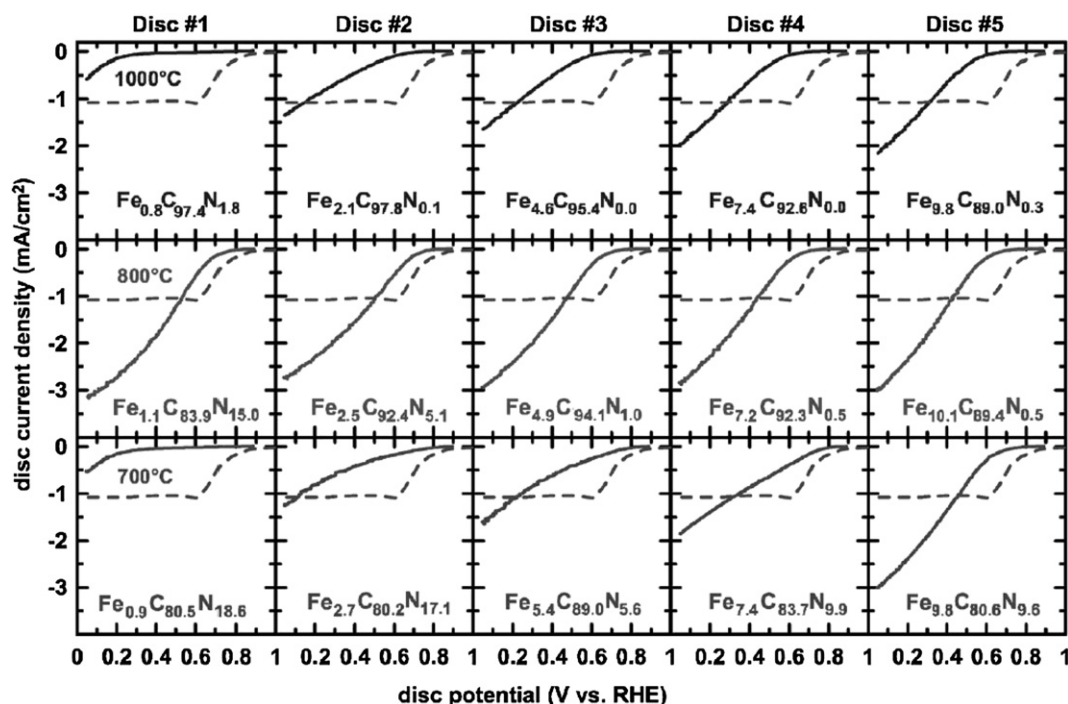
Fig. 12. The ORR activity measurement results of the Fe−C−N arrays annealed at 700, 800, and 1000 °C. The testing was performed at a sweep rate of 5 mV s^{-1} in oxygen saturated 0.1 M HClO$_4$ electrolyte solution at room temperature. Composition of each disk was also shown in the figure. Dashed line is the activity of another previous report [51]. (Reproduction of Fig. 3 of [49]. Reproduced by permission of The Electrochemical Society.)

3. Conclusions

Four approaches for the quick evaluation of combinatorial arrays were reviewed including optical screening, SECM, multielectrode half cell, and multielectrode single cell. Each technique has its own merits and limitations; 1) The optical screening method is the easiest way for a quick search of new catalysts with low cost. But it should be noted that this method measures the ORR activity indirectly and that the evaluation environment (such as pH and effect of indicator) is quite different from real fuel cell conditions. 2) The SECM technique is an excellent tool for the quick evaluation especially when combined with concentrated and small arrays. But the confirmation of the screening results is still required. 3) The multielectrode half cell provides benefits of respective control of each composition and direct measurement of the ORR activity. But stationary set-up of the electrochemical testing station suffers from oxygen depletion on the catalyst surface, and possibility of cross-contamination is questionable. 4) The multielectrode full cell technique is the best method on the point of evaluation as it can provide an ORR activity of each spot in a real fuel cell condition. But an accelerated array fabrication technique should be developed for a higher process yield.

In conclusion, although the combinatorial synthesis and high-throughput screening method cannot provide a perfect solution at this moment, it is clear that this method can accelerate the ORR catalyst research *via* various approaches. And it is important to understand that each method introduced in this review has its own characteristics and to choose a right method for each research condition and purpose.

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